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**Method for the Production of an Ultra-High Molecular
Weight Polyester**

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(54) Title of the Invention: **Method for the Production of an Ultra-High Molecular Weight Polyester**

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SPECIFICATION

1. Title of the Invention

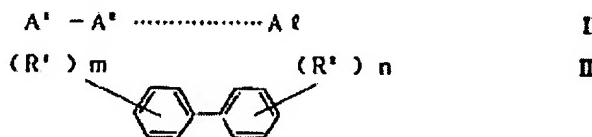
Method for the Production of an Ultra-High Molecular Weight Polyester

2. Claims

(1) A method for the production of an ultra-high molecular weight polyester, characterized in comprising esterification or ester exchange of a glycol and an aromatic

dicarboxylic acid or an alkyl ester thereof; and polycondensation in a heating medium in the presence of a tin compound.

(2) The method for the production of an ultra-high molecular weight polyester according to claim (1), wherein the heating medium is one or two or more compounds selected from compounds represented by the following general formulas I and II:



[In the formulas, A^1 and A^l are phenyl groups or cycloalkyl groups with 5 to 20 carbons, A^2 to A^{l-1} are each a phenylene group or a cycloalkylene group with 5 to 20 carbons, R^1 and R^2 are hydrogen atoms or alkyl groups with 1 to 20 carbons, l is an integer of 2 to 5, and n and m are integers of 0 to 5.]

(3) The method for the production of an ultra-high molecular weight polyester according to claim (1), characterized in that the polycondensation temperature is 235 to 250°C.

(4) The method for the production of an ultra-high molecular weight polyester according to claim (1), characterized in that the polycondensation is performed while inert gas is blown into the system.

(5) The method for the production of an ultra-high molecular weight polyester according to claim (1), characterized in that the polycondensation is performed while a new heating medium is being added and the byproducts are being discharged from the other end.

3. Detailed Description of the Invention

(Field of Industrial Utilization)

The present invention relates to a method for the production of an ultra-high molecular weight polyester. More particularly, it relates to a method for the production of an ultra-high molecular weight polyester from a glycol and an aromatic dicarboxylic acid or an alkyl ester thereof, wherein polycondensation is performed using a specific catalyst in a heating medium.

(Prior Art)

Polyester is usually produced by a process in which an aromatic dicarboxylic acid and a glycol are subjected to direct esterification, or a glycol and an alkyl ester of an aromatic dicarboxylic acid are subjected to ester exchange, to obtain a glycol ester and/or a low polymer thereof, and the product is polycondensed by heating and agitation under a high vacuum.

(Problems That the Invention Is Intended to Solve)

The method of polycondensation by heating and agitation under a high vacuum is currently used on a wide scale in commercial applications, but the method requires vacuum equipment in order to maintain a high vacuum, and strong motive power is needed to agitate highly viscous matter.

Moreover, better physical properties are required of industrial materials such as tire cords, and high molecular weight polyester is therefore being used. It is difficult to agitate this type of higher molecular weight polyester, so the method is usually used whereby the polymer after melt polycondensation is further subjected to solid phase polymerization for a long period of time in an inert gas current. Nevertheless, only a product with a limiting viscosity of 1.0 to 1.5 is usually obtained by this method.

On the other hand, it is also reported that when a polymer is crushed to a fine powder and subjected to solid phase polymerization in an inert gas ambient atmosphere, polyester with a molecular weight of as much as 120,000 is obtained (*Cryogenic Properties of Polymers*, 249, Dekker). It is cited that in this case, the polymer is partially insoluble in the solvent used for viscosity determination, and it is estimated that the molecular weight apparently increases as a result of crosslinking.

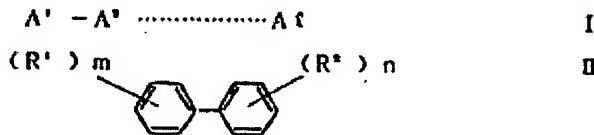
Moreover, a method whereby polyester is polymerized in a solution is cited in USP 2,597,643. However, in this case, the polymerization is performed with the polyester in the form of a completely dissolved solution. This is completely different from the present invention, in which polymerization is performed in a heating medium in which the polyester will swell but

will not dissolve. Furthermore, only polyester with a low limiting viscosity of 0.4 to 0.7 is obtained.

(Means Used to Solve the Above-Mentioned Problems)

The inventors performed intense research in order to solve the above-mentioned problems, and ultimately perfected the present invention as a result of completely revising the prior art. That is, the present invention is a method for the production of an ultra-high molecular weight polyester characterized in comprising esterification or ester exchange of a glycol and an aromatic dicarboxylic acid or an alkyl ester thereof, and polycondensation in a heating medium in the presence of a tin compound.

As used herein, the term "heating medium" refers to an organic compound that is stable in the presence of heat and can be handled as a fluid at the reaction temperature. The heating medium can be a compound or composition selected from aromatic hydrocarbons, aliphatic hydrocarbons, alicyclic hydrocarbons, and aromatic ethers, and the like. However, in the present invention it is preferably a heating medium in which polyester will swell but not dissolve. Preferred examples include one or two or more compounds represented by the following general formulas I and II, particularly triethyl biphenyl, tetraethyl biphenyl, tripropyl biphenyl, diethyl biphenyl, trimethyl biphenyl, cyclohexylbenzene, hydrogenated biphenyl, hydrogenated terphenyl, hydrogenated triphenyl, and the like. It should be noted that the above-mentioned heating medium may also be used after being purified by a conventional method such as distillation or the like.



[In the formulas, A^1 and A^2 are phenyl groups or cycloalkyl groups with 5 to 20 carbons, A^2 to A^l are each a phenylene group or a cycloalkylene group with 5 to 20 carbons, R^1 and R^2 are hydrogen atoms or alkyl groups with 1 to 20 carbons, l is an integer of 2 to 5, and n and m are integers of 0 to 5.]

Terephthalic acid, isophthalic acid, ρ - β -oxyethoxybenzoic acid, 2,6-naphthalenedicarboxylic acid, 4,4'-dicarboxyldiphenyl, 4,4'-dicarboxylbenzophenone, bis(4-carboxyphenyl)ethane, 5-sodium sulfoisophthalic acid, and their alkyl esters such as methyl, ethyl, and propyl esters can be cited as examples of the aromatic dicarboxylic acids or their alkyl esters that are used in the present invention. Ethylene glycol, propylene glycol, butanediol, neopentyl glycol, diethylene glycol, cyclohexane dimethanol, ethylene oxide adducts of bisphenol A, and the like can be cited as examples of suitable glycols.

The tin compound used in the present invention is one that is soluble in polyester. Tin oxides such as stannous oxide and stannic oxide; tin halides such as stannous chloride, stannic chloride, stannous bromide, and stannic bromide; hydrates thereof; and organotin compounds such as di-n-butyltin dichloride, di-n-butyltin oxide, stannous acetate, stannous oxalate, and stannous phosphate can be cited as examples.

In addition, conventional catalysts such as antimony, titanium, germanium, cobalt, manganese, or tungsten compounds can be used together with the above-mentioned tin compound in the present invention.

The polyester production method of the present invention is described below in specific terms. An oligomer is obtained by the esterification or ester exchange of a glycol and an aromatic dicarboxylic acid or its alkyl ester by a conventional method, and then a polyester is obtained by heating and agitating this oligomer (either directly or after initial condensation) for approximately 1 to 20 hours at approximately 200 to 300°C (preferably 235 to 250°C) under normal, reduced, or increased pressure and in the presence of a heating medium and a tin compound. During the reaction, an inert gas (such as nitrogen gas, carbon dioxide gas, helium gas, or argon gas) is blown into the reaction system, and the glycol byproduct that has migrated to the heating medium is removed with by means of the inert gas or by being replaced with a new heating medium.

It should be noted that the polycondensation is performed while the oligomer or polymer in the heating medium is either in a molten state or in a solid state, depending on the heating temperature.

(Operation of the Invention)

Operation of the present invention is as follows. That is, polycondensation of polyester is a reaction that is in equilibrium with the glycol byproduct, and a high molecular weight polymer will not be obtained unless the glycol byproduct is removed from the polymer system. It is believed that the heating medium partially impregnates the polymer and causes it to swell, and that polycondensation is promoted by eliminating the glycol byproduct from the polymer. No explanation has yet been found concerning the unique behavior of the tin compound as a catalyst.

(Working Examples)

The present invention will now be described in specific terms with examples, but the present invention is not limited to these examples.

Working Example 1

Direct esterification of terephthalic acid and ethylene glycol was performed in a reaction vessel with a capacity of 500 mL that was fitted with an agitator with turbine-shaped blades, an inert gas inlet, a gas exhaust outlet, and a bottom discharge port. Then the excess ethylene glycol was removed, and 5 g of the resulting oligomer (containing, as a polymerization catalyst, 0.05 mol% stannous acetate in terms of tin in relation to the acid component; and having a limiting viscosity of 0.34, as determined at 30°C in a phenol/tetrachloroethane 6/4 mixed solvent) and 200 mL of hydrogenated triphenyl as a heating medium were introduced into the reaction vessel and agitated while being kept in a molten state by raising temperature to 240°C as nitrogen gas was blown into the reaction system at 2.0 L/min. Exhaust gas, some of the heating medium, and the ethylene glycol byproduct were discharged from the exhaust outlet, and a new heating medium was added to keep the liquid level constant at this time.

Eight hours later, the polyethylene terephthalate was removed, thoroughly washed with acetone, and dried. The polyester that was obtained was white and had a limiting viscosity of 3.0.

It should be noted that the limiting viscosity referred to in the present invention is the value determined by the following method.

The limiting viscosity, as measured at 30°C using a mixed solvent of p-chlorophenol/tetrachloroethane (3/1), was converted to phenol/tetrachloroethane (6/4) by using the following formula.

$$[\eta]_{60/40 \text{ phenol/TCE}} = 0.8352 \cdot [\eta]_{3/1 \cdot \text{PCP/TCE}} + 0.005$$

Next, the polymer that had deposited on the inside of the reaction vessel was dissolved with 200 mL of m-cresol (it uniformly dissolved with no insoluble matter, and there was no gelling), reprecipitated, washed with methanol, and dried. The limiting viscosity of the polyester that was obtained was 3.0.

Working Example 2

After direct esterification of terephthalic acid and ethylene glycol using the same reaction vessel as in Example 1, conventional melt polymerization was performed. Fifty grams of the resulting oligomer (containing, as a polymerization catalyst, 0.025 mol% stannous acetate in terms of tin in relation to the acid component; and having a limiting viscosity of 0.35) and 250 mL of hydrogenated triphenyl as a heating medium were introduced into the reaction vessel, and the oligomer was directly heated and agitated in a solid phase state while being kept at 237°C by gradually raising the temperature as nitrogen gas was being blown into the reaction system at 2.0 L/minute. The exhaust gas, part of the heating medium, and the ethylene glycol byproduct were discharged from the exhaust outlet during the reaction, and a new heating medium was added to keep the liquid level constant at that time. Twelve hours later, the polyethylene terephthalate was removed, thoroughly washed with acetone, and dried. The polyester that was obtained was pale yellow and had a limiting viscosity of 3.03.

Working Example 3

When exactly the same method as in Working Example 2 was performed with the exception that triethyl biphenyl was used as the heating medium, the limiting viscosity of the polyester that was obtained 12 hours later was 2.79.

(Effect of the Invention)

The use of the method of the present invention whereby polymerization is performed in a heating medium makes a large contribution to industry because it has a variety of advantages, including the following.

- (1) The polymer is swollen by the heating medium, and polymer viscosity decreases, making it unnecessary to use extreme motive force for agitation.
- (2) Polymer pyrolysis and side reactions are prevented because polycondensation can be performed at a low temperature, yielding a high-quality polymer with little coloration.
- (3) A high vacuum is not necessary, dispensing with the need for complex equipment and large amounts of energy.
- (4) Polyester with a high degree of polymerization can be obtained in a simple manner without using conventional solid phase polymerization.

Applicant: Toyobo Co., Ltd.